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<b>(21) International Application Number:</b> PCT/US95/13148 <b>(22) International Filing Date:</b> 18 October 1995 (18.10.95)  <b>(30) Priority Data:</b> 08/331,439 31 October 1994 (31.10.94) US 08/479,963 7 June 1995 (07.06.95) US 08/543,991 17 October 1995 (17.10.95) US  <b>(71) Applicant:</b> W.R. GRACE & CO.-CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036 (US). <b>(72) Inventor:</b> WARD, David, G.; 8408 Woodland Manor Drive, Laurel, MD 20724 (US). <b>(74) Agent:</b> CAPRIA, Mary, Ann; W.R. Grace & Co.-Conn., 7500 Grace Drive, Columbia, MD 21044 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PREPARATION OF MODIFIED POLYOLEFIN CATALYSTS AND IN SITU PREPARATION OF SUPPORTED METAL-LOCENE AND ZIEGLER-NATTA/METALLOCENE POLYOLEFIN CATALYSTS  <b>(57) Abstract</b>  Novel transition and rare earth metal catalysts that do not require the use of alumoxanes, methods for modifying transition or rare earth metal containing compounds that are capable of polymerizing olefinic monomer materials, methods for forming <i>in situ</i> supported metallocenes, supported Ziegler-Natta/metallocene catalysts are provided. Further included is a method for using the novel catalysts to prepare novel polymers.		

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**PREPARATION OF MODIFIED POLYOLEFIN CATALYSTS AND  
IN SITU PREPARATION OF SUPPORTED METALLOCENE  
AND ZIEGLER-NATTA/METALLOCENE  
POLYOLEFIN CATALYSTS**

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This application is a continuation-in-part of U.S. Patent Application Serial No. 08/479,963 filed on June 7, 1995, which is a continuation-in-part of 08/331,439, filed on October 31, 1994.

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Background

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It has been known to use metallocene compounds of transition metals as catalysts for polymerization and copolymerization of olefins. Metallocenes are not polymerization catalysts by themselves, but must be activated with a cocatalyst. The most common cocatalysts are methyl alumoxanes (MAOs), which are oligomeric compounds containing Al-O-Al linkages prepared by the hydrolysis of trimethyl aluminum (TMAL). MAO's are extremely expensive because the TMAL is difficult to prepare and costs an order of magnitude more than the common triethyl aluminum (TEAL) used as a cocatalyst with Ziegler catalysts. MAO's are also more difficult to handle than TEAL due to their inherent instability and the high viscosity of their solutions.

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The use of metallocene catalyst systems provides the ability to produce uniform polymers and copolymers of narrow molecular weight distribution (MWD) and narrow compositional distribution. The use of Ziegler-Natta

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catalyst systems produce resins of a broad MWD and broad compositional distribution.

For many applications, such as extrusion and molding processes, it is highly desirable to have polymers which have a broad molecular weight distribution of the monomodal and/or the multi-modal type. Such polymers evidence excellent processability, i.e., they can be processed at a faster throughput rate with lower energy requirements with reduced melt flow perturbations.

It is known that two or more homogeneous catalysts may be combined to affect properties, such as molecular weight distribution. U.S. Patent No. 4,530,914 discloses use of a catalyst system comprising two or more metallocenes in the polymerization of alpha-olefins, primarily ethylene, to obtain a broad molecular weight distribution. The metallocenes are mixed with an alumoxane to form the catalyst system.

It is also known that metallocenes may be affixed to a support to make a heterogeneous catalyst. U.S. Patent No. 4,808,561 discloses reacting a metallocene with an alumoxane to form a reaction product in the presence of a support. The support is a porous material such as talc, inorganic oxides of Group IIA, IIIA, IVA, or IVB metal oxides such as silica, alumina, silica-alumina, magnesia, titania, zirconia, and mixtures thereof, and resinous material such as polyolefins like finely divided

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polyethylene or polystyrene. The metallocenes and alumoxanes are deposited on the dehydrated support material.

U.S. Patent No. 4,701,432 teaches a support treated with at least one metallocene and at least one non-metallocene transition metal compound. To form a catalyst system, a cocatalyst comprising an alumoxane and an organometallic compound of Group IA, IIA, IIIB, and IIIA is added to the supported metallocene/non-metallocene. The support is a porous solid such as talc or inorganic oxides or resinous material, preferably an inorganic oxide, such as silica, alumina, silica-alumina, magnesia, titania or zirconia, in finely divided form. By depositing the soluble metallocene on the support material, it is converted to a heterogeneous supported catalyst. The transition metal compound, such as  $\text{TiCl}_4$  is contacted with the support material prior to, after, simultaneously with or separately from contacting the metallocene with the support.

A concern in the field of polyolefin manufacture is the ability to control the MWD of the resulting polymer.

Broad MWD have been linked to improved processability and improved performance in the resulting polymer.

Single metallocene catalyst systems typically produce a narrow range of molecular weight. Some techniques such as multiple reactors and physical blending of polymers

have been used in attempt to broaden molecular weight distributions. In other instances, attempts have been made to use admixtures of different catalysts in the same reactor. However, the resulting polymers still require physical blending to obtain a homogeneous material suitable for further processing. EP 0 536 104 discloses a multi-catalyst system that is obtained by mixing the components of at least one homogeneous catalyst and at least one heterogeneous system. The components are physically combined in any order.

Various attempts have been made to improve polymerization processes as well as to better utilize Ziegler and metallocene catalysts in known polymerization processes. Many of the improved processes are so-called gas phase or slurry type processes wherein the catalysts are best used in a supported form. Unfortunately effective supporting of metallocene catalysts on oxide support particles has often been difficult or impossible.

Thus, the potential benefits of these the catalysts in the improved processes can only be realized at significant costs, if at all. Solution, slurry, and gas phase polymerization techniques are well known in the field. See, e.g., Krichelderf, Handbook of Polymer Synthesis, Chapter 1, Part A, p.7-8 (Marcel Dekker 1992).

Thus there remains a need for methods for economically producing a variety of supported polyolefin

catalysts that produce polymers with minimal side reactions and with optimal dispersion of catalytic centers on the support. Moreover, there is a need for a catalyst for olefin polymerization that can be produced  
5 inexpensively while achieving a broad range of molecular weight, bimodal or multi-modal molecular weight distribution in the final polymers.

It is therefore desirable to develop a method that can produce a supported metallocene catalyst or a  
10 combination supported Ziegler-Natta/metallocene catalyst in-situ ("one pot") that does not require the use of expensive MAOs while permitting sufficient process control to optimally and preferentially produce only supported metallocene or the mixed Ziegler-Natta/  
15 metallocene catalyst systems.

It is also desirable to produce a catalyst that is capable of producing polymers with improved processing characteristics such as faster throughput out of  
20 extrusion dies without increasing processing temperature or pressure and polymers with less chlorine residues that corrode polymer processing machinery and lower resin quality. Chlorine in the polymer causes discoloration and deterioration of polymer physical properties.

Accordingly, it is an object of the present  
25 invention to provide novel methods for making supported metallocene in-situ and supported Ziegler-Natta/

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metallocene mixed catalysts in-situ. It is also an object of the present invention to modify existing Ziegler-Natta and chromium catalysts in order to narrow the MWD of the polymer that would have otherwise been produced.

It is a further object of the present invention to provide a metallocene precursor catalyst that eliminates the need to use MAOs and to reduce residual chlorine in the final polymer product.

Additionally, another object of the present invention is to provide a catalyst which is capable of producing polymer with a broad molecular weight.

These and other objects are accomplished by a catalyst produced by the presently disclosed "in-situ method" of catalyst preparation as described below and using the present catalyst in solution, slurry and gas phase polymerization processes to obtain desirable novel polymers. The invention further includes modifying previously prepared polyolefin chromium and Ziegler-Natta catalysts and mixtures thereof with treatment of in-situ reagents.



Summary of the Present Invention

The present invention meets the above objectives by providing improved methods of modifying previously prepared and commercially available polyolefin chromium and Ziegler-Natta catalysts and mixtures thereof as well as manufacturing in-situ supported metallocene and supported Ziegler-Natta/metallocene mixed catalyst precursors.

The invention further provides unique catalyst compositions suitable for forming polymers having broad molecular weight distribution and good flow properties (i.e., the ability to be processed through dies and other machinery without raising the processing temperature or pressure). The polymers produced in accordance with the present invention also have reduced presence of polymer degrading and equipment corroding materials, such as chlorine, in the final polymer product..

In one aspect, the invention encompasses the method to produce a novel catalyst precursor by modifying a previously prepared or commercially available polyolefin catalyst by treatment with the insitu technology defined herein.

In another aspect, the present invention provides a method to prepare in-situ a supported metallocene catalyst and a mixture of ZN/metallocene catalyst

precursors. The method of the present invention comprises:

(A) reacting reagents (i) and (ii) in the presence or absence of a solvent, wherein

5 (i) is a compound that is an organometallic containing a five-member carbon ring, a heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi cyclic moieties capable of coordinating to the transition or rare earth metals, which can be  
10 reacted as an existing, pre-made component or can be created in-situ by combining

(a) a metal containing reagent, wherein the metal in the reagent is selected from the group comprising Groups 1, 2, 3, and 13 metals of the  
15 Periodic Table, Silicon, Germanium, Tin and mixtures thereof, with

(b) an organic compound that contains a five-member carbon ring, a heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as  
20 multi cyclic moieties capable of coordinating to the metals in (i)(a); and

(ii) is a metal containing reagent, wherein the metal component of the reagent is selected from a transition or rare earth metals and mixtures thereof and  
25 the remaining component of the reagent is selected from the group of halogen elements, alkoxides, amides,

organics and mixtures thereof, and optionally, containing an additional organic component that contains a five-member carbon ring, a heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as two  
5 cyclic moieties capable of coordinating to the transition or rare earth metals;

(B) recovering the resulting supported catalyst precursor.

Detailed Description of the Invention

Catalyst precursors of the present invention are useful in the polymerization of any olefin in which separate polymerization with a homogenous catalyst or with a heterogenous catalyst is possible. Preferably, catalysts of the present invention are useful in the polymerization, copolymerization and terpolmerization of olefinic monomers, most preferably,  $\alpha$ -olefins, and most preferably, propylene and ethylene.

The catalyst precursors produced according to the present invention are described below in terms of the manner in which they are made.

The method to prepare supported catalyst precursors according to the present invention can be described by the following graphic representations.

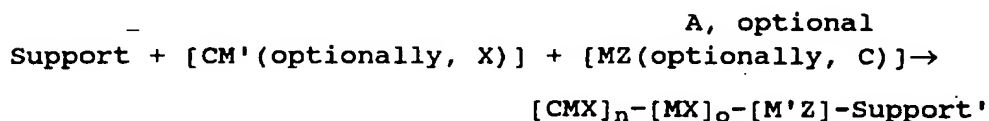
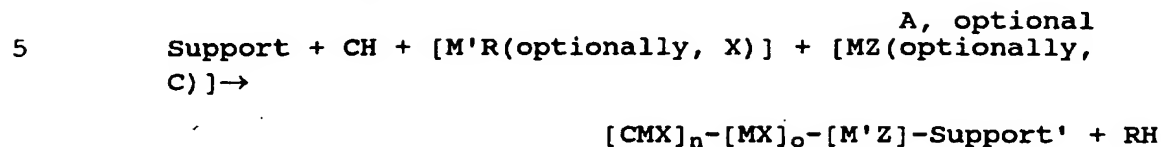
Illustration I (InSitu)

Illustration II (InSitu/InSitu)

The terms used in Illustrations I and II are defined below.

Support

The Support is optional and can be any sufficiently porous inorganic, inorganic oxide or organic material. Suitable inorganic materials include magnesium compounds or their complex salts such as  $\text{MgCl}_2$ ,  $\text{MgCl}(\text{OEt})$  and  $\text{Mg}(\text{OEt})_2$ , organic magnesium compounds such as those represent by  $\text{MgR}'_x\text{X}'_y$  wherein,  $\text{R}'$  is an alkyl group havng 1 to 20 carbon atoms, an alkoxy group having having 1 to 20 carbon atoms or aryl group having 6 to 20 carbon atoms;  $x$  is a halogen atom or an alkyl group having 1 to 20 carbon atoms;  $x$  is a number from 0 to 2; and  $y$  is a number from 0 to 2. Inorganic oxide supports, including talcs, clays, and metal oxides from Groups 2-14, actinide, lanthanide series metals from the Periodic Table; suitable metal oxides are typically  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{ZnO}$ ,  $\text{BaO}$ ,  $\text{ThO}_2$  and mixtures thereof; for example, silica-alumina, silica-titania, silica-titania-alumina, zeolite, ferrite, glass fibers,

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magnesia, titania, zirconia, aluminum phosphate gel, silanized silica and mixtures thereof

Organic Supports include resinous material such as styrene-divinylbenzene copolymers, polyethylene, linear  
5 low density polyethylenes, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyarylates, starches and carbon and mixtures thereof.

Preferably, the carriers are compositions  
10 conventionally used as a catalyst support material. The degree of porosity in the carrier may be any level that is achievable in the starting material. Preferably, the carrier particles of the present invention have a pore volume of at least 0.1 cc/g; preferably more than 1.0  
15 cc/g; and more preferably from about 0.3 to 5 cm<sup>3</sup>/g. Preferably, the carrier particles have a surface area of about 1-1000 m<sup>2</sup>/g; more preferably in the range of from 100 - 800 m<sup>2</sup>/g; and more preferably 250-600 m<sup>2</sup>/g. The  
20 typical median particle size for a suitable carrier for this invention is from 1 to 300 microns, preferably from 15 to 200 microns, more preferably from 25 to 150 microns.

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Pore volume and surface area, for example, can be measured from volume of nitrogen gas adsorbed in accordance with BET method. (Refer to J. Am. Chem. Soc., Vol. 60, p. 309 (1983)).

5

C

C represents a ligand defined as one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi-cyclic moieties capable of coordinating to the transition or rare earth metals, M.

10

The ansa bridge can be selected from the group comprising carbon, silicon, phosphorus, sulfur, oxygen, nitrogen, germanium, species such as  $R''_2C$ ,  $R''_2Si$ ,  $R''_2Ge$ ,  $R''_2CR''_2C$ ,  $R''_2SiR''_2Si$ ,  $R''_2GeR''_2Ge$ ,  $R''_2CR''_2Si$ ,  $R''_2C R''_2Ge$ ,  $R''_2CR''_2CR''_2C$ ,  $R''_2SiR''_2Si$ , diradicals where R is independently selected from the group containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals including ethyl, propyl; preferred ansa bridges include  $Me_2Si$  (dimethylsilyl),  $-Ph_2Si$  (diphenylsilyl),  $Me_2C$  (isopropylidene),  $Ph_2P$  (diphenylphosphoryl),  $Me_2SiSiMe_2$  (tetramethyldisilane) and the like. Preferably, the ansa bridge has a length of two atoms or less as in methylene, ethylene, diphenylsilyl, dimethylsilyl, and methylphenylsilyl.

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M'

M' represents a metal selected from the group comprising Group 1, 2, 3 and 13 metals of the Periodic Table; preferably, Mg, Al, Zn, In, silicon, germanium, tin and mixtures thereof; and most preferably, Mg, Al, Zn, Si, Sb and mixtures thereof; wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is at least 1:1; and preferably 2:1 or greater.

M

M represents a metal selected from the group consisting of Groups 3 through 10, lanthanides, actinides metals of the Periodic Table and mixtures thereof; preferably titanium, zirconium, hafnium, chromium, vanadium, and samarium and neodymium and mixtures thereof; most preferably Ti, Zr, and Hf, and mixtures thereof.

The definition of MZ is intended to include any existing Ziegler-Natta catalytic precursors.

X and Z

X and Z represents elements from the halogen group (preferably chlorine, fluorine, bromine and mixtures thereof), and halosubstituted and non-substituted alkoxys (preferably C1-C20 alkoxys, such as methoxy, ethoxy, isopropoxy, butoxy and phenoxy); alkyls (preferably C1-



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C20 alkyls such as ethyl, butyl, octyl, ethylhexyl);  
aryls (preferably C6-C20 aryls such as phenyl, p-tolyl,  
benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-  
methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl);  
5 alkenyls (preferably C1-C20 alkenyls, such as ethenyl,  
propenyl, butenyl, pentenyl); amides (preferably  $\text{NR}^a\text{R}^b$ ,  
wherein the  $\text{R}^a$  and  $\text{R}^b$  can be the same or different and  
independently selected from halosubstituted and non-  
substituted alkyls, alkenyls, aryls, or silanes;  
10 preferably C1-C20 alkyls and alkenyls and C6-C20 aryls,  
including substituted aryls, such as ethyl, butyl, octyl,  
ethylhexyl), phenyl, p-tolyl, benzyl, 4-t-butylphenyl,  
2,6-dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl,  
2,3-dimethylphenyl); preferred amides are dimethylamide,  
15 diethylamide, hexamethyldisilazide and mixtures of two or  
more of the foregoing. More preferred R groups in the  
 $\text{NR}^a\text{R}^b$  are C1-C5 alkyls, C2-C5 alkenyls, phenyl and Naphthyl  
and mixtures thereof.

X and Z may be the same or different and are  
20 preferably chloride, bromide, ethoxy, and mixtures  
thereof; wherein n is never 0. The n and o refer to  
quantity (wt.% or molar ratio) and not the number of any  
particular ligand. When o is zero, a supported  
metallocene catalytic precursor system is achieved. When  
25 n is any number greater than zero, a supported mixed

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Ziegler-Natta ("ZN")/metallocene catalytic precursor system is achieved;

H in Illustration II represents hydrogen;

R in Illustration II represents any component  
5 capable of deprotonating the C, resulting in in-situ  
preparation of CM. R is preferably mono or multi-cyclic  
halosubstituted and nonsubstituted aryls, alkyls, and  
alkenyl groups and mixtures thereof; preferred are C1-20  
alkenyl groups (such as ethene, propylene, butene, and  
10 pentene); C1-20 alkyl groups (such as a methyl, ethyl, n-  
propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl  
groups), C6-20 aryl group (including substituted aryls)  
(such as phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6-  
dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl,  
15 2,3-dimethylphenyl groups) and mixtures thereof. R may  
also be an amide  
(preferably  $\text{NR}^a\text{R}^b$ , wherein the  $\text{R}^a$  and  $\text{R}^b$  can be the same  
or different and independently selected from alkyls,  
alkenyls, aryls, or silanes; preferably C1-C20 alkyls and  
20 alkenyls and C6-C20 aryls, including substituted aryls,  
such as ethyl, butyl, octyl, ethylhexyl), phenyl, p-  
tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-  
methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl);  
more preferred R groups in the  $\text{NR}^a\text{R}^b$  are C1-C5 alkyls, C2-  
25 C5 alkenyls, phenyl and naphthyl and mixtures thereof.

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Preferred amides are dimethylamide, diethylamide, hexamethyldisilazide and mixtures of two or more of the foregoing.

5 PREFERRED CM'X AND CM', respectively

CM'X is preferably selected from the group comprising dicyclopentadienylethylaluminum, bis(pentamethylcyclopentadienyl)aluminumchloride, cyclopentadienylmagnesium chloride, dicyclopentadienyl  
10 aluminumchloride, cyclopentadienylaluminumdichloride, dicyclopentadienylmagnesium, bisindenylethylaluminum, indenylmagnesiumchloride, bisindenylaluminum chloride, indenylaluminumdichloride, diindenylmagnesium, difluorenylethylaluminum, difluorenylaluminum,  
15 fluorenylmagnesiumchloride, difluorenylaluminumchloride, fluorenylaluminumdichloride, difluorenylmagnesium and mixtures thereof.

A

20 A, may be optionally used to further modify the catalyst and/or support, and can be selected from the group comprising acid halides, (e.g., HCl, HBr and HI); metal halides (preferably, Al, Si, Sn, Ti, Mg, Cr wherein the halide are Cl, Br, I and mixtures thereof; organic  
25 halides (R'X), carboxcyclic acids (R'(COOH)<sub>n</sub>), esters (R'(COOR'')<sub>n</sub>), ethers (R'(OR'')<sub>n</sub>) when n is equal to or

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greater than 1, alcohols wherein the R' and R'' are the same or different and independently selected from mono or multi-cyclic halosubstituted and non-substituted aryls, alkyls, and alkenyl groups and mixtures thereof; preferred are C1-20 alkenyl groups (such as ethenyl, propylenyl, butenyl, and pentenyl); C1-20 alkyl groups (such as a methyl, ethyl, n-propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl groups), C6-20 aryl group (including substituted aryls) (such as phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6 dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl groups) and mixtures thereof. More preferred R groups are C1-5 alkyls, C2-5 alkenyls, phenyl and naphthyl and mixtures thereof.

"A" can also be C1-C20 alkylaluminums (preferably C1-C10 alkylaluminums, and most preferably triethyl aluminum, trimethylaluminum, tributylaluminum and mixtures thereof); C1-C20 alkyl lithium (preferably, C1-C6 alkyl lithium, and most preferably n-butyllithium, methyllithium, ethyllithium and mixtures thereof); and Grignard reagents, generally represented by the formula  $RMgX$ , where X is selected from the members of the halogen group from the Periodic Table, R is selected from the group comprising a C1-C20 alkyls and C6-C20 aryls, preferably C1-C6 alkyls and C6-C10 aryls, preferred Grignard reagents are methyl magnesium chloride, ethyl

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magnesium chloride, and isopropyl magnesium bromide and mixtures thereof.

Additional suitable "A" compounds for use in this invention are halogen gas and alumoxanes.

5 Preferred A's include  $\text{CH}_3\text{Cl}$ , tetrahydrofuran, dibutylphthalate, t-butylchloride, dialkyl phthalates, ethanol, phenol, ethylaluminumdichloride, silicon tetrachloride, methyllithium, methylmagnesium chloride, dibutylphthalate, dibutylphthalate and tin tetrachloride;  
10 halogen gases such as  $\text{Cl}_2$ ,  $\text{F}_2$ , and  $\text{Br}_2$  and mixtures of two or more of the foregoing.

#### SUPPORT'

The Support' can be the same as the Support (before any reaction takes place) or can be a modified Support as  
15 a result of the occurring reaction. For example, when trimethylsilylcyclopentadiene ("TMSCp") or other silanizing agents are used, the silanizing agent reacts with the support to consume any residual hydroxyl that may be present.

20 Conditions of the reaction can vary causing the reaction product to be completely metallocene or a mixed ZN/metallocene catalyst system. The reaction can be carried over a broad range of temperatures, typically from approximately  $-78^\circ\text{C}$  to  $200^\circ\text{C}$ , preferably at  $0^\circ\text{C}$  to  
25 room temperature.

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The reaction product will typically have the following compositional characteristic. The values provided below are given in weight percent of the final dry catalyst.

5           CMX is approximately 0.1% to 50%; preferably 0.1 - 10%; most preferably 0.1-5.0%;

          MX is approximately 0.0% to 50%; preferably 0.0-20%; most preferably 0.5-10%;

          M'Z is approximately 0.1% to 99.8%; preferably 5.0- 10 50%; most preferably 5-15%; and

          Support' is approximately 0.0% to 99.8%.

          In Illustrations I and II described above, the M'Z acts as a support and can be thought of as a co-support to the reagent "Support'." Each reaction can be carried 15 out without the addition of Support, wherein the co-support, M'Z, is created in-situ and acts as the only support for the catalyst. Thus, Support' is absent.

          The method further includes using any composition containing a transition metal or rare earth metal capable 20 of polymerizing olefinic monomers. These are typically preformed polyolefin catalysts such as a chromium catalyst, Ziegler-Natta catalyst, metallocene catalyst (including supported) and physical mixtures thereof, which are modified by reactively treating with the CM'X 25 to a obtain reaction product that is a new supported olefin catalyst.

This reaction is illustrated by Illustration III as follows.

ILLUSTRATION III

[Preformed metallocenic, Ziegler-Natta  
and/or Cr Catalysts,  
which may be supported,  
thereby containing  
MZ(optionally, C)] + [CM'(optional, X)]<sub>n</sub> → Modified  
Preformed  
Catalyst

Illustrations I, II, and III above are carried out in the presence of a solvent in either a solution or a slurry. The solvents that are desirably utilized are solvents that do not adversely affect the preparation of the catalyst or, if any residue remains, does not adversely affect polymerization or the properties of the resulting polymer. Preferably, the solvent is a non-polar organic solvent; and most preferably includes aliphatic hydrocarbons (typically C3 to C12, such as butane, isobutane, pentane, isopentane, hexane, octane, decane, dodecane, hexadecane, octadecane, and the like); alicyclic hydrocarbons (typically C5-C20, such as cyclopentane, methylcyclopentane, cyclohexane, decalin cyclooctane, norbornane, ethylcyclohexane and the like); aromatic hydrocarbons, including substituted aromatics such as benzene, chlorobenzene, xylene, toluene and the like; and petroleum fractions such as gasoline, kerosene, light oils, and the like. It may also be desirable to

use tetrahydrofuran or another ether. Mixtures of two or more solvents may also be used, e.g., Exxon's IsoPar ®.

The method can be controlled to achieve a supported metallocene or a supported mixed ZN/metallocene catalyst system through selection of reagents, stoichiometry, temperature and other reaction conditions such as solvent used and time allowed for the reaction.

#### PREFERRED PRODUCTS CMX

The starting materials can be selected as defined above to achieve the CMX that is a metallocene catalytic precursor defined as organometallic compounds having a transition metal, including rare earth metals, in coordination with members of at least one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi cyclic moieties capable of coordinating to the transition or rare earth metals.

The ansa bridge can be selected from the group comprising carbon, silicon, phosphorus, sulfur, oxygen, nitrogen, germanium, species such as,  $R^3_2C$ ,  $R^3_2Si$ ,  $R^3_2Ge$ ,  $R^3_2CR^3_2C$ ,  $R^3_2SiR^3_2Si$ ,  $R^3_2GeR^3_2Ge$ ,  $R^3_2CR^3_2Si$ ,  $R^3_2CR^3_2Ge$ ,  $R^3_2CR^3_2CR^3_2C$ ,  $R^3_2SiR^3_2Si$  diradicals where  $R^3$  is independently selected from the group containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals including ethyl and propyl; preferred ansa bridges are  $Me_2Si$  (dimethylsilyl),  $Ph_2Si$  (diphenylsilyl),  $Me_2C$

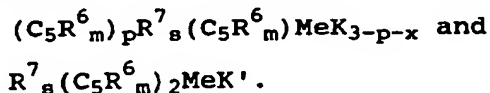


(isopropylidene),  $\text{Ph}_2\text{P}$  (diphenylphosphoryl)  $\text{Me}_2\text{SiSiMe}_2$  (tetramethyldisilane) and the like. Preferably, the ansa bridge has a length of two atoms or less as in methylene, ethylene, diphenysilyl, dimethylsilyl, propylidene and methylphenylsilyl.

The transition metal component of the metallocene is selected from Groups 3 through 10, lanthanides and actinides series of the Periodic Table and mixtures thereof; and most preferably, titanium, zirconium, hafnium, chromium, vanadium, samarium and neodymium and mixtures thereof. Of these Ti, Zr, and Hf and mixtures thereof are most preferable.

In one preferred embodiment, the CMX metallocene catalyst precursor is represented by the general formula  $(\text{Cp})_m \text{MR}^4_n \text{R}^5_p$ , wherein Cp is a substituted or unsubstituted cyclopentadienyl ring, M is a Group 3-6, lanthanide, actinide series metal from the Periodic Table and mixtures thereof;  $\text{R}^4$  and  $\text{R}^5$  are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms;  $m=1-3$ ,  $p=0-3$  and the sum of  $m+n+p$  equals the oxidation state of M.

In another embodiment the CMX is represented by the formulae:



Wherein Me is a Group 3-6, lanthanide, actinide series metal from the Periodic Table and mixtures thereof;  $C_5R_m^6$  is a substituted cyclopentadienyl each  $R^6$ , which can be the same or different is hydrogen, alkenyl, aryl, or arylalkyl radical having from 1 to 20 carbon atoms or two carbon atoms joined together to form a part of a C4 to C6 ring;  $R^7$  is one or more of or a combination of a carbon, a germanium, a silicon, a phosphorous or a nitrogen atom containing radical substitution on and bridging two  $C_5R_m^6$  rings or bridging one  $C_5R_m^6$  ring back to Me, when  $p=0$  and  $x=1$  otherwise  $x$  is always equal to 0, each K which can be the same or different is an aryl alkyl, alkenyl, alkaryl, or arylalkyl radical having from 1-20 carbon atoms or halogen, K' is an alkylidene radical having from 1 to 20 carbon atoms,  $s$  is 0 to 1 and when  $s$  is 0,  $m$  is 5 and  $p$  is 0, 1, or 2 and when  $s$  is 1,  $m$  is 4 and  $p$  is 1.

In particular, preferred metallocenes are derivatives of a cyclopentadiene (Cp), including cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, and 1,1-disubstituted silacyclopentadienes, phosphocyclopentadienes, 1-metallocyclopenta-2,4-dienes, bis(indenyl)ethane and mixtures thereof.

Additional illustrative, but non-limiting, examples of metallocenes represented by the above definition are dialkyl metallocenes such as bis(cyclopentadienyl)titanium

dimethyl, bis(cyclopentadienyl)titanium diphenyl,  
bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium dimethyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl,  
5 bis(cyclopentadienyl)zirconium di neopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl)titanium phenyl  
10 chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)titanium methyl bromide; the trialkyl metallocenes such as  
15 cyclopentadienyl titanium trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium trineopentyl, cyclopentadienyl zirconium trimethyl, cyclopentadienyl hafnium triphenyl, cyclopentadienyl hafnium trineopentyl, and cyclopentadienyl hafnium  
20 trimethyl; monocyclopentadienyls titanocenes such as, pentamethylcyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium trichloride; bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene represented by the formula bis(cyclopentadienyl)titanium=CH<sub>2</sub> and derivatives of this reagent; substituted  
25 bis(cyclopentadienyl)titanium (IV) compounds such as:



ntadienyl) (fluorenyl)hafnium dichloride, diisobutylmethyle  
ne(cyclopentadienyl) (fluorenyl)hafnium dichloride,  
ditertbutylmethylene(cyclopentadienyl) (fluorenyl)hafnium  
dichloride, cyclohexylidene(cyclopentadienyl) (fluorenyl)haf  
5 nium dichloride, diisopropylmethylene(2,5-  
dimethylcyclopentadienyl) (fluorenyl)hafnium  
dichloride, isopropyl(cyclopentadienyl) (fluorenyl)titanium  
dichloride, diphenylmethylene(cyclopentadienyl)  
(fluorenyl)titanium dichloride, diisopropylmethylene(cyclop  
10 entadienyl) (fluorenyl)titanium dichloride,  
diisobutylmethylene(cyclopentadienyl) (fluorenyl)titanium  
dichloride, ditertbutylmethylene(cyclopentadienyl)  
(fluorenyl)titanium dichloride, cyclohexylidene(cyclopentad  
ienyl) (fluorenyl)titanium dichloride,  
15 diisopropylmethylene(2,5 fluorenyl)titanium dichloride,  
racemic-ethylene bis (1-indenyl) zirconium (IV) dichloride,  
racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl)  
zirconium (IV) dichloride, racemic-dimethylsilyl  
bis (1-indenyl) zirconium (IV) dichloride, racemic-  
20 dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) zirconium  
(IV) dichloride, racemic-1,1,2,2- tetramethylsilanylene bis  
(1-indenyl) zirconium (IV) dichloride, racemic-1,1,2,2-  
tetramethylsilanylene bis (4,5,6,7-tetrahydro-1- indenyl)  
zirconium (IV), dichloride, ethylidene (1-indenyl  
25 tetramethylcyclopentadienyl) zirconium (IV) dichloride,  
racemic- dimethylsilyl bis (2-methyl-4-t-butyl-1-

cyclopentadienyl) zirconium (IV) dichloride, racemic-  
ethylene bis (1-indenyl) hafnium (IV) dichloride, racemic-  
ethylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV)  
dichloride, racemic-dimethylsilyl bis (1-indenyl) hafnium  
5 (IV) dichloride, racemic-dimethylsilyl (4,5,6,7-tetrahydro-  
1- indenyl) hafnium (IV) dichloride, racemic-1,1,2,2-  
tetramethylsilanylene bis (1-indenyl) hafnium(IV)  
dichloride, racemic-1,1,2,2-tetramethylsilanylene bis  
(4,5,6,7-tetrahydro-1- indenyl) hafnium (IV), dichloride,  
10 ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-  
cyclopentadienyl) hafnium (IV) dichloride, racemic-  
ethylene bis (1-indenyl) titanium (IV) dichloride, racemic-  
ethylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV)  
dichloride, racemic- dimethylsilyl bis (1-indenyl) titanium  
15 (IV) dichloride, racemic- dimethylsilyl bis (4,5,6,7-  
tetrahydro-1-indenyl) titanium (IV) dichloride, racemic-  
1,1,2,2-tetramethylsilanylene bis (1-indenyl) titanium (IV)  
dichloride racemic-1,1,2,2-tetramethylsilanylene bis  
(4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride,  
20 and ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-  
cyclopentadienyl) titanium IV) dichloride.

Preferred CMX's are bis(cyclopenta-dienyl)titanium  
dichloro, bis(cyclopentadienyl)zirconium,  
isopropyl(cyclopentadienyl)fluoroenyl)zirconium dichloro, bis  
25 (1-indenyl) zirconium (IV) dichloro, (4,5,6,7-tetrahydro-1-  
indenyl)hafnium(IV)dichloro, dimethylzirconene,

dichloroethylenebisindenylzirconium, and dichloroethylene bis(tetrahydroindenyl)zirconium.

The CMX in this invention can also include non-cyclopentadienyl catalyst components (such as  
5 pentadienyls) as well as ligands such as borollides or carbollides in combination with a transition metal.

#### POLYMERIZATION

The catalytic precursors prepared according to the  
10 method of the present invention may be activated by any number of catalytic activators and used to polymerize olefinic materials.

The catalytic activators includes those represented by the formula  $R_n^4 AlX_{3-n}$  where  $R^4$  is a hydrocarbon radical  
15 having from 1 to about 20 carbon atoms, X is monovalent radical selected from the halogens and hydrogen, and n is an integer of 0-3. Examples of specific compounds include trimethylaluminum, triisobutylaluminum, tridodecylaluminum, tricyclohexyl aluminum,  
20 triphenylaluminum, tribenzylaluminum, diethylaluminum chloride, ethylaluminum dichloride, isopropylaluminum dibromide, diisobutylaluminum hydride, and the like, and mixtures thereof.

While unnecessary to practice the present invention,  
25 the catalytic activator may also include alumoxanes, such

as C1-C8 alkyl alumoxanes such as methylalumoxane, isobutylalumoxane and mixtures thereof.

Additional suitable catalytic activators for use with this invention are represented by the formulae:

5  $[C^+]^- [N^n(Q_1-Q_{n+1})]$  and  $N^n(Q_n)$ .

$[C^+]$  is an activating cation, which may be a Bronsted acid capable of donating a proton to the transition metal ionic catalytic precursor resulting in a transition metal cation. Such Bronsted acids include but  
10 are not limited to ammoniums, oxoniums, phosphoniums and mixtures thereof; preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo-  
15 N,N,-dimethylaniline, p-nitro-N,N-dimethylaniline; phosphoniums from triethylphosphine, triphenylphosphine and diphenylphosphine; oxoniums from ethers such as diethyl ether, tetrahydrofuran and dioxane; sulfoniums from thioethers such as diethyl thioethers and  
20 tetrahydrothiophene; mixtures thereof; most preferably dimethylanilinium and mixtures thereof.

Furthermore,  $[C^+]$  may be an abstracting moiety that is capable of reacting with a transition metal catalytic precursor resulting in the transition metal cation.  
25 Acceptable abstracting moiety include but are not limited to silver, carbocations, tropylium, carbeniums,



ferroceniums and mixtures thereof; preferably carboniums and ferroceniums and mixtures thereof; and most preferably triphenyl carbenium. The  $[C^+]$  may also include mixtures of the Bronsted acids and the abstracting moiety species.

[N] is selected from the group consisting of boron, phosphorus, antimony or aluminum and mixtures thereof, having the n valence state. Preferably, the [N] is boron, aluminum and mixtures thereof.

$[Q_1-Q_{n+1}]$  are independent, wherein  $Q_1-Q_{n+1}$  are RX is defined wherein X is a halogen group element and is typically fluorine, chlorine, and bromine and mixtures thereof; preferred halogens are fluorine, chlorine, iodine and mixtures thereof; and most preferred is fluorine; and R is mono or multi-cyclic aryls, alkyls, and alkenyl groups and mixtures thereof; preferred are C1-20 alkenyl groups (such as ethene, propylene, butene, and pentene); C1-20 alkyl groups (such as a methyl, ethyl, n-propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl groups), C6-20 aryl group (including substituted aryls) (such as phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6 dimethylphenyl, 3,5- methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl groups) and mixtures thereof. More preferred R groups are C1-5 alkyls, C2-5 alkenyls phenyl and naphthyl and mixtures thereof.

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Preferred RX compounds are C1-20 halogenated hydrocarbon groups such as  $XCH_2$ ,  $X_2CH$ ,  $X_3C$ ,  $C_2X_nH_{n-5}$  (where  $n = 1-5$ ),  $C_3H_nX_{n-7}$  ( $n = 1-7$ ) and  $C_6X_nH_{n-6}$  ( $n = 1-6$ ) and mixtures thereof; most preferably,  $FCH_2$ ,  $CHF_2$ ,  $F_3C$ , and fluorosubstituted phenyl, wherein the phenyl can be mono to pentasubstituted (such as p-fluorophenyl, 3,5-difluorophenyl, pentafluorophenyl, 3,4,5-trifluorophenyl, and 3,5-bis(trifluoromethyl)phenyl groups) and mixtures thereof; of these the most preferred is pentafluorophenyl.

Moreover, in this RX, the  $Q_1$  to  $Q_n$  may be hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, substituted hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl- and halocarbyl-substituted organometalloid radicals. Additionally, the  $Q_1$  to  $Q_n$  can simply be the X alone; for example as in  $\bar{B}X_4$ .

In addition, neutral  $N^n(Q_n)$ , can be used in place of the  $[C^+][N^n(Q_1-Q_{n+1})]$ , for example  $B(C_6F_5)_3$ .

Preferred  $[N^n(Q_1-Q_{n+1})]$  are selected from the group consisting of  $\bar{B}Phenyl_4$ ,  $\bar{B}(C_6H_2(CF_3)_3)_4$ ,  $\bar{B}(C_6H_5)_4$ ,  $\bar{Al}Phenyl_4$ ,  $\bar{Al}(C_6H_2(CF_3)_3)_4$ ,  $\bar{Al}(C_6H_5)_4$ ,  $\bar{PF}_6$ ,  $\bar{BF}_4$ ,  $\bar{B}(OPh)_4$  and mixtures thereof; preferably  $\bar{B}(C_6F_5)_4$ ,  $\bar{Al}(C_6F_5)_4$ ,  $\bar{Al}(C_6H_2(CF_3)_3)_4$ ,  $\bar{Al}(C_6H_5)_4$ ,  $\bar{BC}_6H_2(CF_3)_3)_4$  and mixtures thereof; most preferred are  $\bar{B}(C_6F_5)_4$ ,  $\bar{Al}(C_6F_5)_4$

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and mixtures thereof. Preferred  $N^n(Q_n)$  from the neutral species of the preferred list above of  $[N^n(Q_1-Q_{n+1})]$ .

Most preferred catalytic activators are organo aluminum co-catalysts such as TEAL, tri-methylaluminum, tri-isobutylaluminum, tri-n-octylaluminum, ethylaluminum dichloride, diethylaluminumchloride and the like; ionic cocatalysts from the boron family such as tris(pentafluorophenyl)borane, dimethylanilinium tetra(pentafluorophenyl)borate, triphenylcarbenium tetra(pentafluorophenyl)borate, and the like; and cocatalysts from the aluminate family such as dimethylanilinium tetra(pentafluorophenyl)aluminate, triphenylcarbenium tetra(pentafluorophenyl)aluminate and the like in conjunction with an alkylating agent such as an alkylaluminum or other organometallic and mixtures of all of the above activators.

The present invention is capable of polymerizing olefinic materials in a slurry phase polymerization reactor, such as a 2L Zipperclave under conditions as described in the examples below, achieving a catalytic activity of at least 10 grams of polyethylene per 1g catalyst used, without the use of an alkylalumoxane catalytic activator.

In general, however, the catalytic systems using the present invention are useful to polymerize olefinic materials, particularly ethylene. Polymerizations of

olefinic monomers can be accomplished by any number of well known techniques by having the olefinic material come into contact with the polymerization catalyst(s) in a reaction zone under appropriate conditions.

5           As used herein, "Polymerization" includes copolymerization and terpolymerization and the terms olefins and olefinic monomer includes olefins, alpha olefins, diolefins, strained cyclic olefins, styrenic monomers, acetylenically unsaturated monomers, cyclic  
10           olefins alone or in combination with other unsaturated monomers. While the catalyst system of the present invention is active for this broad range of olefinic monomer feedstock, alpha-olefin polymerizations is preferred, especially the homopolymerization of ethylene  
15           and propylene or the copolymerization of ethylene with olefins having 3 to 10 carbon atoms.

          "Polymerization techniques" for olefin polymerization according to the present invention can be solution polymerization, slurry polymerization or gas  
20           phase polymerization techniques. Method and apparatus for effecting such polymerization reactions are well known and described in, for example, Encyclopedia of Polymer Science and Engineering published by John Wiley and Sons, 1987, Volume 7, pages 480-488 and 1988, Volume  
25           12, pages 504-541. The catalyst according to the present invention can be used in similar amounts and under

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similar conditions to known olefin polymerization catalyst.

Typically, for the slurry process, the temperature is from approximately 0 degrees C to just below the temperature at which the polymer becomes soluble in the polymerization medium. For the gas phase process, the temperature is from approximately 0 degrees C to just below the melting point of the polymer. For the solution process, the temperature is typically the temperature from which the polymer is soluble in the reaction medium up to approximately 275 degrees C.

The pressure used can be selected from a relatively wide range of suitable pressures, e.g., from subatmospheric to about 350 Mpa. Suitably, the pressure is from atmospheric to about 6.9 Mpa, or 0.05-10 Mpa, especially 0.14-5.5 Mpa. In the slurry or particle form process, the process is suitably performed with a liquid inert diluent such as a saturated aliphatic hydrocarbon. Suitably the hydrocarbon is a C4 to C10 hydrocarbon, e.g., isobutane, heptane or an aromatic hydrocarbon liquid such as benzene, toluene or xylene. The polymer is recovered directly from the gas phase process or by filtration or evaporation from the slurry process or evaporation from the solution process.

The catalyst of the present invention are particularly suited for the gas phase or slurry process.

The compositions according to the present invention are used in amounts sufficient to cause polymerization in the feedstocks. Typically, the amount used will be the range of 0.0005 mmole to 10 mmole/liter of reactor; most preferably from 0.01 mmole to 2.5 mmole/liter of reactor.

The following examples are provided to illustrate the present invention, but are not to be construed as limiting the invention in any way except as provided in the appended claims.

10

## EXAMPLES

In the following examples, the reactions were carried out using a mixture of silica gel and dicyclopentadienyl magnesium to which titanium tetrachloride is added. Gaseous HCl was passed through the solution for approximately thirty seconds to provide a deep red slurry. The solvent was removed in vacuo. The orange solid was analyzed by DRIFTS and solid state <sup>13</sup>C-NMR. This analysis revealed that there was negligible remaining hydroxyl content and the absorbance due to the cyclopentadienyl ring coordinated to titanium is clearly visible. The NMR spectra has a small amount of residual heptanes solvent but only one signal, identified by shift, corresponding to a titanocene dichloride.

The addition of further titanium tetrachloride will produce a Ziegler-Natta catalyst co-supported with the metallocene catalyst.

Example 1-7 ("In-Situ Method")

A 20g aliquot of the desired support is weighed into a flask in an argon purged glove box. The sealed flask is removed from the glove box and the support is slurried in approximately 200ml of hexane under an argon atmosphere using typical Schlenk techniques. The slurry is shaken at 0°C and a slurry of di(cyclopentadienyl)magnesium ("Cp<sub>2</sub>Mg") is added. The amounts of the reagents are shown in Table A. Neat TiCl<sub>4</sub>, is added and the mixture shaken an additional 15 minutes at 0°C. The resulting slurry is shaken overnight at room temperature.

A 10 second burst of HCl gas is admitted to the slurry and it is shaken an additional 15 minutes. The supernatant is decanted and the solids washed with three, 75 ml aliquots of hexanes. The remaining solvents are removed in vacuo. The catalysts were used to polymerize olefins and the results are shown in Table C.

TABLE A

Ex.	SiO <sub>2</sub> (g)	Cp <sub>2</sub> Mg (g)	TiCl <sub>4</sub> (ml)	Mg (mmol/g)	Ti (mmol/g)	Mg/Ti
1	20*	3.1	2.2	0.175	0.0875	2.0
2	20.4**	3.1	2.2	0.165	0.0825	2.0
3	20**	6.2	2.2	0.325	0.0875	3.7
4	20*	6.2	2.2	0.3175	0.0825	3.8
5	20**	6.2	0.5	0.39	0.0325	12.0
6	20.2*	6.2	0.5	0.375	0.025	15.0
7	0	6.2	0.4	1.4	0.2075	6.7

\* = silanized

\*\* = calcined at 800 degrees C.



Example 1-7a--Comparison of In-Situ Preparation with  
In-Situ treated with a Ziegler-Natta

5           The catalysts of samples 1, 2, 3, 5, 6, and 7 were  
treated with 0.3 ml of  $\text{TiCl}_4/\text{g}$  catalyst and washed thrice  
with excess hexanes. The catalysts were used to  
polymerize olefins and the results are shown in Table C,  
10 as samples 1a, 2a, 3a, 5a, 6a, and 7a.

Examples 8-11("In-Situ-In-Situ Method")

15           A 20g aliquot of the desired support is weighed into  
a flask in an argon purged glove box. The sealed flask  
is removed from the glove box and the support is slurried  
in approximately 200ml of hexanes under an argon  
atmosphere using typical Schlenk techniques. The slurry  
is shaken at  $0^\circ\text{C}$  and of Cyclopentadiene is added. The  
20 amounts of the reagents are shown in Table B. At  $0^\circ\text{C}$ ,  
dialkylmagnesium ( $\text{R}_2\text{Mg}$ ) is added. The slurry is shaken  
for 1 hour at  $0^\circ\text{C}$  and an additional 2 hours at room  
temperature. Neat  $\text{TiCl}_4$  is added and the mixture shaken  
an additional 15 minutes at  $0^\circ\text{C}$ . The resulting slurry is  
25 shaken overnight at room temperature. A 10 second burst  
of  $\text{HCl}$  gas is admitted to the slurry and it is shaken an  
additional 15 minutes. The supernatant is decanted and  
the solids washed with three 75 ml aliquots of hexanes.  
The remaining solvents are removed in vacuo.

TABLE B

Sample	SiO <sub>2</sub> (g)	CpH (ml)	R <sub>2</sub> Mg (mmol)	TiCl <sub>4</sub> (ml)	Mg (mmol/g)	Ti (mmol/g)	Mg/Ti
8	20**	20	120	1.1	0.625	0.03625	17.2
9	20.1*	20	120	1.1	0.6325	0.0475	13.3
10	20**	6.6	40	4.4	---	---	--
11	20*	6.6	40	4.4	---	---	--

\* = silanized

\*\* = calcined at 800 degrees C.

Example 8a-11a -- Comparison of In-Situ/In-Situ Preparation with In-Situ treated with a Ziegler-Natta

The catalysts of samples 8, 9, 10 and 11 were treated with 0.3 ml of TiCl<sub>4</sub>/g catalyst and washed thrice with excess hexane solvent. The catalysts were used to polymerize olefins and the results are shown in Table C, as samples 8a, 9a, 10a, and 11a.

TABLE C  
Polymerization Results

Sample	Yield* (g)	Sample**	Yield* (g)
1	10	1a	6.2
2	0.1	2a	0.2
3	6.0	3a	4.4
4	6.0		
5	0.3	5a	1.7
6	0.15	6a	6.5
7	4.3	7a	10.6
8	0.9	8a	5.8
9	0.55	9a	2.7
10	8.5	10a	17.7
11	15.0	11a	16.6

\* Yield = Grams of Polyethylene  
 \*\* Sample Post Treated with  $\text{TiCl}_4$

Examples 12 and 12a -- Comparison  $\text{Cp}_2\text{Mg}$  MODIFIED  
 PREFORMED CATALYST To UNMODIFIED CATALYST

A commercial silica supported Ziegler/Natta catalyst,  
 $[(\text{TiCl}_4)\text{MgCl}_2\text{-SiO}_2]$  was prepared separately and modified  
 with  $\text{Cp}_2\text{Mg}$  by mixing the ZN catalyst with the  $\text{Cp}_2\text{Mg}$  in  
 hexane, making a metallocene catalyst precursor on the  
 surface of the support. Polymers were prepared using the  
 preformed ZN catalyst and with the modified ZN catalyst  
 prepared in accordance with this invention and the  
 results are shown in samples 12 and 12a in Table D,  
 respectively. The activity of the modified ZN catalyst  
 is double the activity of the preformed, unmodified ZN

catalyst and the MWD of the resulting polymer narrower.

TABLE D

Sample	Yield(g)	MWD
12	12	Fig. 1, 65
12a	23	Fig. 2, 9

5

Example 13

Silanized silica catalyst support (20g) was slurried in hexanes (150 mL) and cooled to 0°C under an atmosphere of dry, deoxygenated argon. To this slurry, 10 dibutylmagnesium (40 mmol) was added followed, in 30 minutes, by cyclopentadiene (80 mmol). This slurry was mixed a further 2 hours at room temperature and recooled to 0°C. Neat TiCl<sub>4</sub> (40 mmol) was added. After mixing 16 15 hours at RT, the slurry was exposed to HCl(g) for 30 seconds. The liquid phase was removed and the solid portion washed with hexanes (3 times with 75 mL). The solids were dried in vacuo at 50°C.

Elemental Analyses: 5.5 wt% Ti, 2.6 wt% Mg

20

Example 14 -- Comparative Example of Physical Mixture of Metallocene

Silanized support (10g) was slurried in THF (70 mL) 25 and titanocene dichloride (20 mmol) and magnesium

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dichloride (20 mmol) as THF solutions were added. The slurry was mixed 1 hour at RT and dried in vacuo at 50°C.

General Polymerization Protocol  
for Examples 15 through 25

5 A 2 litre Zipperclave<sup>®</sup> is purged with purified argon at 100°C for one hour. Heptane (500 mL) containing TEAL (500 mmol) and desired comonomer is added. The reactor  
10 is saturated with the desired partial pressure of H<sub>2</sub> (60 psig unless otherwise noted) followed by ethylene up to 180 psig. After temperature equilibration is reached, the catalyst as a slurry in heptane (c. 20 mL) with TEAL (500 mmol) cocatalyst (or activator) is blown in under  
15 argon pressure. Ethylene uptake and temperature are monitored. The polymerization is quenched by rapid release of the ethylene pressure followed by argon purging. The polymer is washed with MeOH, stabilized and dried for more than 16 hours in vacuo. In no case, when  
20 products of the present invention were utilized, was any fouling of the reactor noted.

Examples 15-18 and 20-25 use a catalyst system incorporated the in-situ prepared Ex. 13 and TEAL as its activator. Examples 19 is physical mixture catalyst of  
25 Ex. 14 activated with TEAL.

Al/Ti Ratio Effects on Sample 13

Ex.	Al (mmol)	Cat (g)	Ti (mmol)	Al/Ti	A
15	0.5	0.052	0.060	8	1.3
16	2	0.014	0.016	120	7
17	10	0.052	0.060	170	2

A=activity in kg PE/g cat-h  
Activator is triethylaluminum.

5

Comparative Example(Ex. 13 vs. Ex. 14)

Ex	Al (mmol)	Cat (g)	Ti (mmol/g)	Ti (mmol)	Al/Ti	P (C2=)	t (h)	Y (g)	A
18, using Ex. 13	1	0.052	1.15	0.060	20	180	1	135	3
19, using Ex. 14	1	0.058	1.16	0.067	20	180	1	16	0.3

A=activity in kg PE/g cat-h

Extensive reactor fouling resulted from the use of Example 14 catalyst (Example 19, herein).

10

Copolymerization (Ex. 13 Catalyst) with 1-Hexene

Ex	Al (mmol)	Cat (g)	Ti (mmol)	Al/Ti	Y (g)	A	MI	HLMI	MFR	mp	dH
20	1	0.052	0.060	17	168	3	0.44	13	29	132.5	184.2

15 mL of 1-hexene added to reactor;

A=activity in kg PE/g cat-h

MI = Melt Index, (ASTM Procedure 1238, Condition E)

HLMI = High Load Melt Index (ASTM Procedure 1238, condition F)

MFR = Melt Flow Ratio (ASTM Procedure 1238)

15

Varying Hydrogen Partial Pressure Using Ex. 13 Catalyst

Ex	Al (mmol)	Cat (g)	Ti (mmol/g)	Ti (mmol)	Al/ Ti	P (H <sub>2</sub> )	P (C <sub>2</sub> =)	Y (g)	A
21	2	0.017	1.15	0.020	102	0	180	120	7
22	2	0.014	1.15	0.016	124	10	170	130	9
23	2	0.014	1.15	0.016	124	30	150	90	6
24	2	0.014	1.15	0.016	124	60	120	96	7
25	2	0.015	1.15	0.017	116	90	90	18	1.2

A=activity in kg PE/g cat-h

Figure 1 depicts a chromatogram of a polyethylene  
 5 produced by a commercial Ziegler-Natta catalyst (Ex. 12).

Figure 2 depicts the resulting chromatogram of PE  
 produced with the present invention: the catalyst used in  
 Fig. 1 was treated with Cp<sub>2</sub>Mg prior to polymerization of  
 10 ethylene (Ex. 12a).

Figure 3 depicts the chromatogram of polyethylene  
 produced with the present invention in Example 22.

Figure 4 depicts the chromatogram of polyethylene  
 15 produced with the present invention in Example 15.

**COMPOSITIONAL ANALYSIS**

20 In order to prove the difference in character of  
 these two materials, each material was washed in separate  
 Soxhlet extractors and extracted with toluene for a

period of 2.5 hours at reflux. The results are provided below.

CHARACTERISTIC	Example 13	Example 14
INITIAL COLOR	DARK GREEN-BROWN	PINK
FINAL COLOR	GRAY-GREEN	LIGHT BROWN
INITIAL WEIGHT	2.00	2.00
FINAL WEIGHT	1.93	1.31
% LOSS	3.5	35

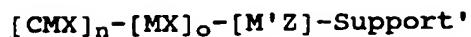
5           The loss on extraction is an order of magnitude less for Ex. 13, is the present invention.

          Likewise, repeating the same experiment in THF the physical mixture material, Ex. 14, was reduced to pure silica upon extraction with the tetrahydrofuran (THF).  
10       These two experiments indicate the material achieved in accordance with the present invention is not the same as that prepared using the normal techniques to prepare supported metallocene catalyst precursors.



## I CLAIM:

1. A supported polyolefin catalytic precursor comprising comprising:



5 wherein,

Support' is selected from the group comprising porous inorganic, inorganic oxide or organic material;

C is defined as one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi-cyclic moieties capable of coordinating to the transition or rare earth metals, M;

10 M is selected from the group comprising Groups 3 through 10, lanthanides, actinides metals of the Periodic Table and mixtures thereof;

15 M' is selected from the group comprising Group 1, 2, 3 and 13 metals of the Periodic Table, wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is at least 1:1;

20 X and Z may be the same or different are selected from the group comprising halogen group elements, halosubstituted and non-substituted alkoxys, alkyls, aryls, alkenyls, amides and mixtures of any two or more of the foregoing X's and Z's; and

25 wherein the composition has the following characteristics CMX is approximately 0.1% to 50%;

MX is approximately 0.0% to 50%;

M'Z is approximately 0.1% to 99.8%; and

Support' is approximately 0.0% to 99.8%.

- 5           2.    The composition according to Claim 1, wherein  
              Support' is selected from the group comprising  
MgCl<sub>2</sub>, MgCl(OEt), Mg(OEt)<sub>2</sub>, organic magnesium compounds  
represent by MgR'<sub>x</sub>X'<sub>y</sub> wherein, R' is is an alkyl group  
havng 1 to 20 carbon atoms, an alkoxy group having having  
10           1 to 20 carbon atoms or aryl group having 6 to 20 carbon  
atoms; x is a halogen atom or an alkyl group having 1 to  
20 carbon atoms; x is a number from 0 to 2; and y is a  
number from 0 to 2, talcs, clays, and metal oxides from  
Groups 2-14, actinide, lanthanide series metals, styrene-  
15           divinylbenzene copolymers, polyethylene, linear low  
density polyethylenes, polypropylene, polyvinylchloride,  
polyvinylalcohol, poly-4-methyl-1-pentene, substituted  
polystyrenes and polyarylates, starches and carbon and  
mixtures thereof;
- 20           C has an ansa bridge selected from the group  
comprising carbon, silicon, phosphorus, sulfur, oxygen,  
nitrogen, germanium, species such as R''<sub>2</sub>C, R''<sub>2</sub>Si,  
R''<sub>2</sub>Ge, R''<sub>2</sub>CR''<sub>2</sub>C, R''<sub>2</sub>SiR''<sub>2</sub>Si, R''<sub>2</sub>GeR''<sub>2</sub>Ge, R''<sub>2</sub>CR''<sub>2</sub>2Si,  
R''<sub>2</sub>C R''<sub>2</sub>Ge, R''<sub>2</sub>CR''<sub>2</sub>CR''<sub>2</sub>C, R''<sub>2</sub>SiR''<sub>2</sub>Si, diradicals  
25           where R is independently selected from the group

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containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals;

M is selected from the group comprising titanium, zirconium, hafnium, chromium, vanadium, samarium, neodymium and mixtures thereof; and

M' is selected from the group comprising preferably, Mg, Al, Zn, In, silicon, germanium, tin and mixtures thereof, wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is 2:1 or greater;

X and Z are selected from the group comprising C1-C20 alkoxys, C1-C20 alkyls, C6-C20 aryls, C1-C20 alkenyls, amides of the formula  $NR^aR^b$ , wherein the  $R^a$  and  $R^b$  can be the same or different and independently selected from halosubstituted and non-substituted alkyls, alkenyls, aryls, or silanes, and mixtures of two or more of the foregoing X's or Z's; and

wherein the composition has the following characteristics CMX 0.1 - 10%; MX is 0.0-20%; and MZ is 5.0-50%.

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3. The composition according to claim 2, wherein, Support' is selected from the group  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{ZnO}$ ,  $\text{BaO}$ ,  $\text{ThO}_2$  and mixtures thereof;

5 C has an ansa bridge selected from the group comprising dimethylsilyl, diphenylsilyl, isopropylidene, diphenylphosphoryl, tetramethyldisilane, methylphenylsilyl, methylene, ethylene and mixtures thereof;

10 M' is selected from the group comprising Mg, Al, Zn, Si, Sb and mixtures thereof;

X and Z are selected from the group comprising methoxy, ethoxy, isopropoxy, butoxy, phenoxy, ethyl, butyl, octyl, ethylhexyl, phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl, ethenyl, propenyl, 15 butenyl, pentenyl, dimethylamide, diethylamide, hexamethyldisilazide and mixtures of two or more of the foregoing; and

20 wherein the composition has the following characteristics CMX is 0.1-5.0%; MX is 0.5-10%; and MZ is 5-15%.

25

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4. The composition according to claim 3, wherein  
Support' is selected from the group comprising  
silica-alumina, silica-titania, silica-titania-alumina,  
5 zeolite, ferrite, glass fibers, magnesia, titania,  
zirconia, aluminum phosphate gel, silanized silica and  
mixtures thereof;

C is dicyclopentadienyl;

M' is Mg;

10 M is Ti; and

X and Z are selected from the group comprising  
chloride, bromide, and mixtures thereof, wherein n is  
never 0.

15 5. A method for preparing a supported polyolefin  
catalytic precursor, said method comprising the steps of  
reacting reagents (i) and (ii) wherein

(i) is an organometallic compound of the formula  
CM', and (ii) is represented by the formula MZ, wherein

20 C is defined as one five-member carbon ring,  
heterosubstituted five-member carbon ring, or a bridged  
(ansa) ligand defined as multi-cyclic moieties capable of  
coordinating to the transition or rare earth metals, M;

M is selected from the group comprising Groups 3  
25 through 10, lanthanides, actinides metals of the Periodic  
Table and mixtures thereof;

M' is selected from the group comprising Group 1, 2, 3 and 13 metals of the Periodic Table, wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is at least 1:1;

X and Z may be the same or different are selected from the group comprising halogen group elements, halosubstituted and non-substituted alkoxys, alkyls, aryls, alkenyls, amides and mixtures of any two or more of the foregoing X's and Z's; and

wherein the reagents are used in an amount sufficient to result in a reaction composition having the following characteristics CMX is approximately 0.1% to 50%;

MX is approximately 0.0% to 50%; and  
M'Z is approximately 0.1% to 99.8%.

6. The method according to claim 5, wherein C has an ansa bridge selected from the group comprising carbon, silicon, phosphorus, sulfur, oxygen, nitrogen, germanium, species such as  $R''_2C$ ,  $R''_2Si$ ,  $R''_2Ge$ ,  $R''_2CR''_2C$ ,  $R''_2SiR''_2Si$ ,  $R''_2GeR''_2Ge$ ,  $R''_2CR''_2Si$ ,  $R''_2C R''_2Ge$ ,  $R''_2CR''_2CR''_2C$ ,  $R''_2SiR''_2Si$ , diradicals where R is independently selected from the group containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals;

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M is selected from the group comprising titanium, zirconium, hafnium, chromium, vanadium, samarium, neodymium and mixtures thereof; and

5 M' is selected from the group comprising preferably, Mg, Al, Zn, In, silicon, germanium, tin and mixtures thereof, wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is 2:1 or greater;

10 X and Z are selected from the group comprising C1-C20 alkoxys, C1-C20 alkyls, C6-C20 aryls, C1-C20 alkenyls, amides of the formula  $NR^aR^b$ , wherein the  $R^a$  and  $R^b$  can be the same or different and independently selected from halosubstituted and non-substituted alkyls, alkenyls, aryls, or silanes, and mixtures of two or more  
15 of the foregoing X's or Z's; and

wherein the reagents are selected to result in a reaction composition having the following characteristics  
CMX 0.1 - 10%; MX is 0.0-20%; and MZ is 5.0-50%.

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7. The method according to claim 6 wherein  
C has an ansa bridge selected from the group  
comprising dimethylsilyl, diphenylsilyl, isopropylidene,  
diphenylphosphoryl, tetramethyldisilane,  
5 methylphenylsilyl, methylene, ethylene and mixtures  
thereof;

M' is selected from the group comprising Mg, Al, Zn,  
Si, Sb and mixtures thereof;

10 X and Z are selected from the group comprising  
chlorine, fluorine, methoxy, ethoxy, isopropoxy,  
butoxy, phenoxy, ethyl, butyl, octyl, ethylhexyl, phenyl,  
p-tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl,  
3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl,  
ethenyl, propenyl, butenyl, pentenyl, dimethylamide,  
15 diethylamide, hexamethyldisilazide and mixtures of two or  
more of the foregoing; and

wherein the reagents are selected in an amount  
sufficient to result in a reaction composition having the  
following characteristics CMX is 0.1-5.0%; MX is 0.5-10%;  
20 and MZ is 5-15%.

8. The method according to claim 7 wherein  
C is dicyclopentadienyl;  
M' is Mg;  
25 M is Ti; and  
X and Z are chlorine.



9. The method according to Claims 5-8, wherein the reactants further including a Support selected from the from the group comprising  $MgCl_2$ ,  $MgCl(OEt)$ ,  $Mg(OEt)_2$ ,  
5 organic magnesium compounds represent by  $MgR'_xX'_y$  wherein,  $R'$  is is an alkyl group havng 1 to 20 carbon atoms, an alkoxy group having having 1 to 20 carbon atoms or aryl group having 6 to 20 carbon atoms;  $x$  is a halogen atom or an alkyl group having 1 to 20 carbon atoms;  $x$  is  
10 a number from 0 to 2; and  $y$  is a number from 0 to 2, talcs, clays, and metal oxides from Groups 2-14, actinide, lanthanide series metals, styrene-divinylbenzene copolymers, polyethylene, linear low density polyethylenes, polypropylene, polyvinylchloride,  
15 polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyarylates, starches and carbon and mixtures thereof;

$CM'$  may contain  $X$  defined the same as  $Z$  and  $MZ$  may further contain  $C$ .

20

10. The method according to Claims 5-9 wherein the reagents further include A group comprising acid halides, metal halides, organic halides, carboxcyclic acids, esters, ethers, C1-C20 alkyaluminums, C1-C20 alkyl  
25 lithium, Grignard reagents, halogen gas, alumoxanes and mixtures thereof.

11. The method according to claim 10 wherein A is selected from the group comprising HCL, HBr, HI, metal  
5 halides of Al, Si, Sn, Ti, Mg, Cr and mixtures thereof wherein the halide are Cl, Br, I and mixtures thereof; triethyl aluminum, trimethylaluminum, tributylaluminum, n-butyllithium, methyllithium, ethyllithium, methyl  
magnesium chloride, ethyl magnesium chloride, and  
10 isopropyl magnesium bromide, chlorine gas and mixtures of two or more of the foregoing.

12. The method according to claims 5-11 wherein CM and CMX, respectively, is selected from the group  
15 comprising dicyclopentadienylethylaluminum, bis(pentamethylcyclopentadienyl)aluminumchloride, cyclopentadienylmagnesium chloride, dicyclopentadienyl aluminumchloride, cyclopentadienylaluminumdichloride, dicyclopentadienylmagnesium, bisindenylethylaluminum,  
20 indenylmagnesiumchloride, bisindenylaluminum chloride, indenylaluminumdichloride, diindenylmagnesium, difluorenylethylaluminum, difluorenylaluminum, fluorenylmagnesiumchloride, difluorenylaluminumchloride, fluorenylaluminumdichloride, difluorenylmagnesium and  
25 mixtures thereof.

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13. A method for preparing a supported polyolefin catalytic precursor, said method comprising the steps of reacting reagents (i), (ii), and (iii) wherein

(i) is an organometallic compound of the formula CH, and (ii) is represented by the formula M'R, and (iii) is MZ, wherein

C is defined as one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi-cyclic moieties capable of coordinating to the transition or rare earth metals, M;

M is selected from the group comprising Groups 3 through 10, lanthanides, actinides metals of the Periodic Table and mixtures thereof;

M' is selected from the group comprising Group 1, 2, 3 and 13 metals of the Periodic Table, wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is at least 1:1;

H is hydrogen;

R is

X and Z may be the same or different are selected from the group comprising halogen group elements, halosubstituted and non-substituted alkoxys, alkyls, aryls, alkenyls, amides and mixtures of any two or more of the foregoing X's and Z's; and

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wherein the reagents are used in an amount sufficient to result in a reaction composition having the following characteristics CMX is approximately 0.1% to 50%;

5           MX is approximately 0.0% to 50%; and  
          M'Z is approximately 0.1% to 99.8%.

14. The method according to claim 13, wherein  
C has an ansa bridge selected from the group  
10 comprising carbon, silicon, phosphorus, sulfur, oxygen,  
nitrogen, germanium, species such as R''<sub>2</sub>C, R''<sub>2</sub>Si,  
R''<sub>2</sub>Ge, R''<sub>2</sub>CR''<sub>2</sub>C, R''<sub>2</sub>SiR''<sub>2</sub>Si, R''<sub>2</sub>GeR''<sub>2</sub>Ge, R''<sub>2</sub>CR''<sub>2</sub>Si,  
R''<sub>2</sub>C R''<sub>2</sub>Ge, R''<sub>2</sub>CR''<sub>2</sub>CR''<sub>2</sub>C, R''<sub>2</sub>SiR''<sub>2</sub>Si, diradicals  
where R is independently selected from the group  
15 containing hydride, halogen radicals, and C1-20  
hydrocarbyl radicals;

M is selected from the group comprising titanium,  
zirconium, hafnium, chromium, vanadium, samarium,  
neodymium and mixtures thereof; and

20           M' is selected from the group comprising preferably,  
Mg, Al, Zn, In, silicon, germanium, tin and mixtures  
thereof, wherein M' always contains an amount of Mg, Al,  
Zn and mixtures thereof such that the molar ratio of  
these elements in M' to M is 2:1 or greater;

25           X and Z are selected from the group comprising C1-  
C20 alkoxys, C1-C20 alkyls, C6-C20 aryls, C1-C20

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alkenyls, amides of the formula  $NR^aR^b$ , wherein the  $R^a$  and  $R^b$  can be the same or different and independently selected from halosubstituted and non-substituted alkyls, alkenyls, aryls, or silanes, and mixtures of two or more  
5 of the foregoing X's or Z's; and

wherein the reagents are selected to result in a reaction composition having the following characteristics  
CMX 0.1 - 10%; MX is 0.0-20%; and MZ is 5.0-50%.

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15. The method according to claim 14 wherein  
C has an ansa bridge selected from the group  
comprising dimethylsilyl, diphenylsilyl, isopropylidene,  
diphenylphosphoryl, tetramethyldisilane,  
5 methylphenylsilyl, methylene, ethylene and mixtures  
thereof;

M' is selected from the group comprising Mg, Al, Zn,  
Si, Sb and mixtures thereof;

10 X and Z are selected from the group comprising  
chlorine, fluorine, methoxy, ethoxy, isopropoxy,  
butoxy, phenoxy, ethyl, butyl, octyl, ethylhexyl, phenyl,  
p-tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl,  
3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl,  
ethenyl, propenyl, butenyl, pentenyl, dimethylamide,  
15 diethylamide, hexamethyldisilazide and mixtures of two or  
more of the foregoing; and

wherein the reagents are selected in an amount  
sufficient to result in a reaction composition having the  
following characteristics CMX is 0.1-5.0%; MX is 0.5-10%;  
20 and MZ is 5-15%.

16. The method according to claim 15 wherein  
C is dicyclopentadienyl;  
M' is Mg;  
25 M is Ti; and  
X and Z are chlorine.

17. The method according to Claims 13-16, wherein the reactants further including a Support selected from the from the group comprising  $\text{MgCl}_2$ ,  $\text{MgCl}(\text{OEt})$ ,  $\text{Mg}(\text{OEt})_2$ , organic magnesium compounds represent by  $\text{MgR}'_x\text{X}'_y$  wherein,  $\text{R}'$  is is an alkyl group havng 1 to 20 carbon atoms, an alkoxy group having having 1 to 20 carbon atoms or aryl group having 6 to 20 carbon atoms;  $x$  is a halogen atom or an alkyl group having 1 to 20 carbon atoms;  $x$  is a number from 0 to 2; and  $y$  is a number from 0 to 2, talcs, clays, and metal oxides from Groups 2-14, actinide, lanthanide series metals, styrene-divinylbenzene copolymers, polyethylene, linear low density polyethylenes, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyarylates, starches and carbon and mixtures thereof;

$\text{CM}'$  may contain  $\text{X}$  defined the same as  $\text{Z}$  and  $\text{MZ}$  may further contain  $\text{C}$ .

18. The method according to Claims 13-17 wherein the reagents further include A group comprising acid halides, metal halides, organic halides, carboxcyclic acids, esters, ethers,  $\text{C1-C20}$  alkyaluminums,  $\text{C1-C20}$  alkyl lithium, Grignard reagents, halogen gases, alumoxanes and mixtures thereof.

19. The method according to claim 18 wherein A is selected from the group comprising HCL, HBr, HI, metal halides of Al, Si, Sn, Ti, Mg, Cr and mixtures wherein the halide are Cl, Br, I and mixtures thereof; triethyl aluminum, trimethylaluminum, tributylaluminum, n-butyllithium, methyllithium, ethyllithium, methyl magnesium chloride, ethyl magnesium chloride, and isopropyl magnesium bromide, chlorine gas and mixtures of two or more of the foregoing.

20. The method according to claims 5-11 wherein C is selected from the group comprising cyclopentadienyl, fluorenyl, tetrahydroindenyl, dicyclopentadienylethyl, bis(pentamethylcyclopentadienyl), cyclopentadienyl, cyclopentadienyl, bisindenylethyl, indenyl, diindenyl, and mixtures thereof.

21. The product produced by the method of claims 5 through 20.

22. A process for polymerizing olefinic monomer material comprising contacting one or more olefinic compounds with one or more catalysts defined by claims 1 through 21, in the presence of a catalyst activator in a



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reaction zone, thereby polymerizing said olefinic compounds.

5           23. The process according to claim 22, wherein the reaction zone occurs in a slurry, solvent or gas phase polymerization reactor.

10           24. A polymer formed by polymerizing olefinic material in the presence of one or more catalysts as defined in claims 1-4 and a catalyst activator.

15           25. A polymer formed by polymerizing olefinic material in the presence of one or more catalysts prepared in accordance with claims 5 through 20 and a catalyst activator.

FIG. 1

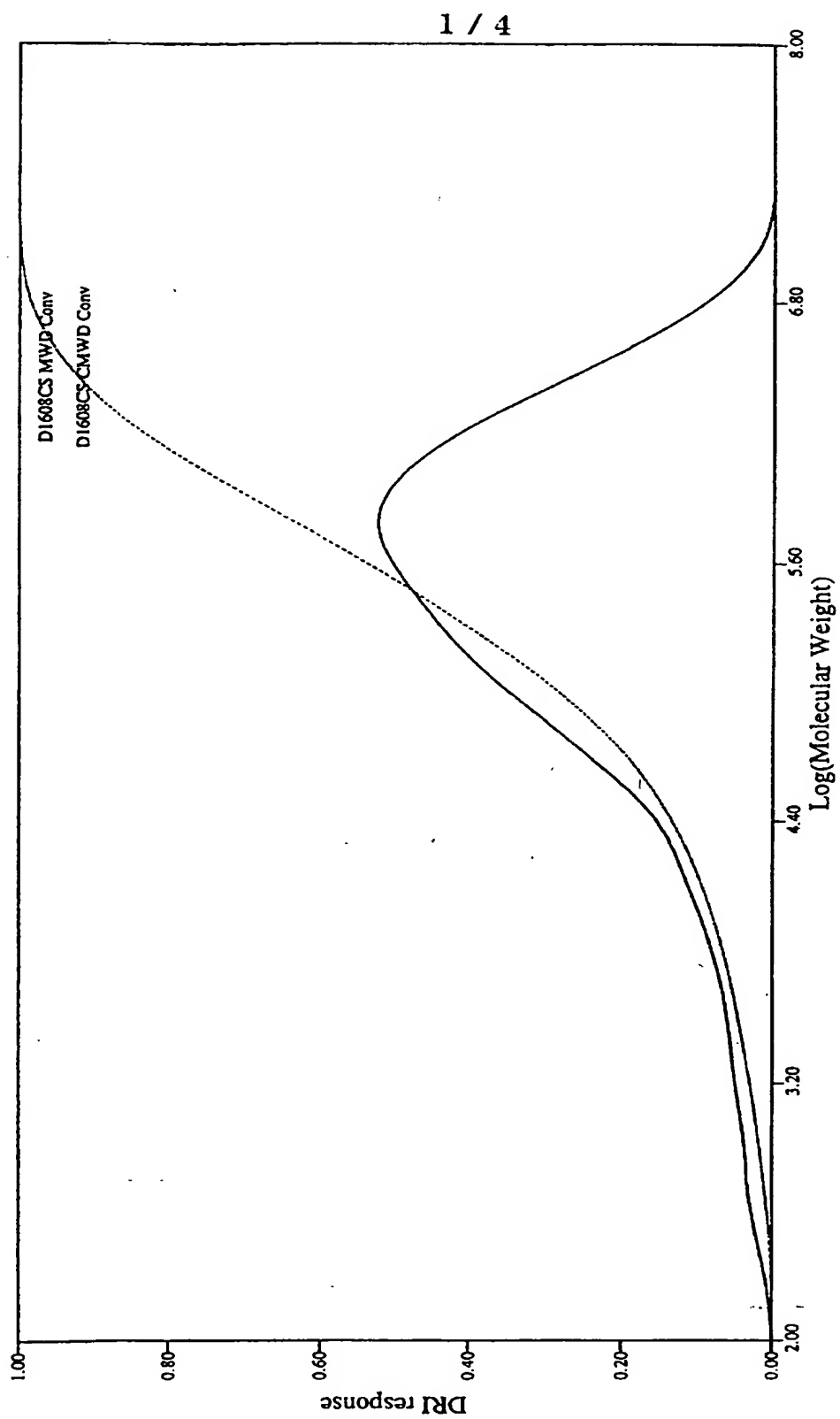
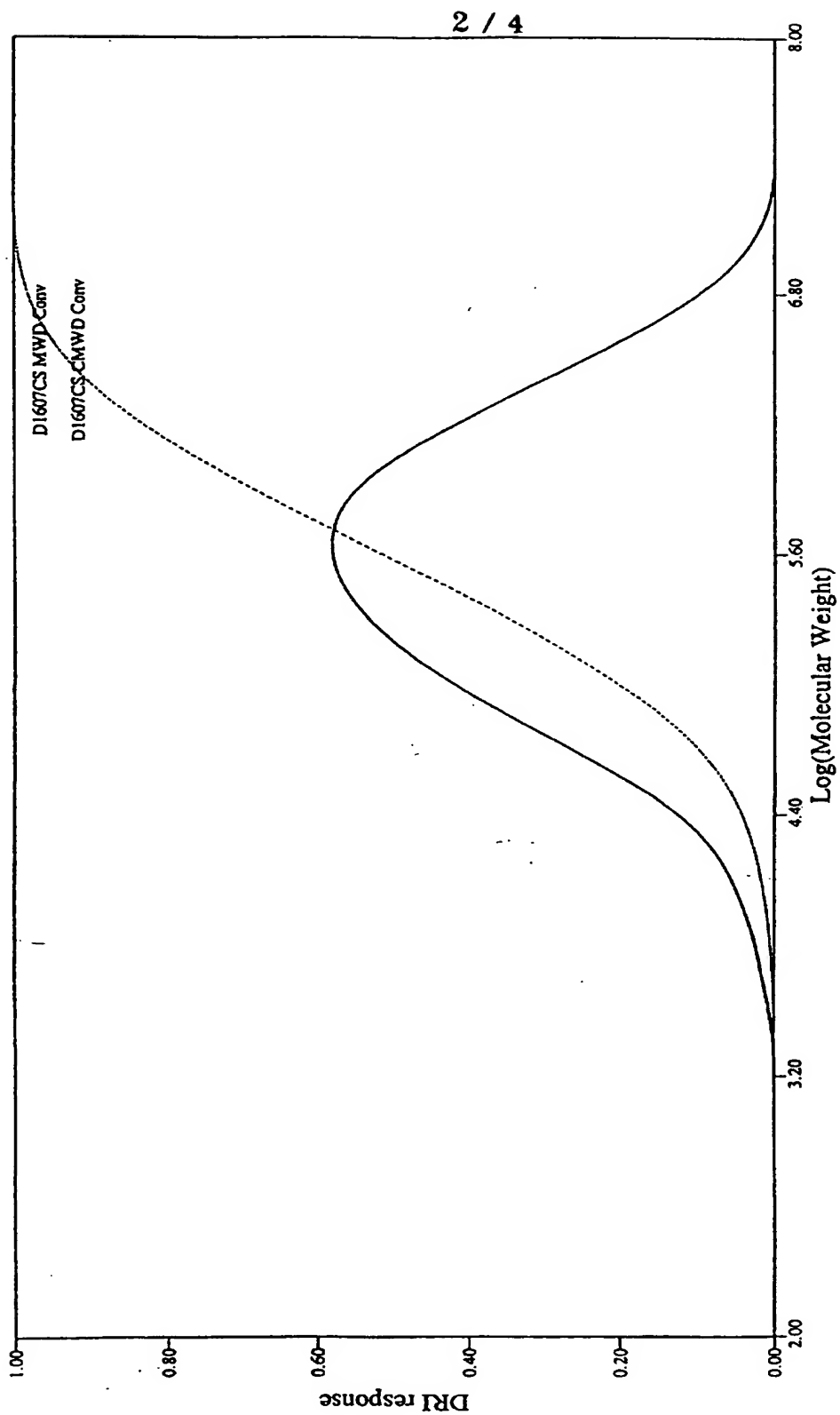
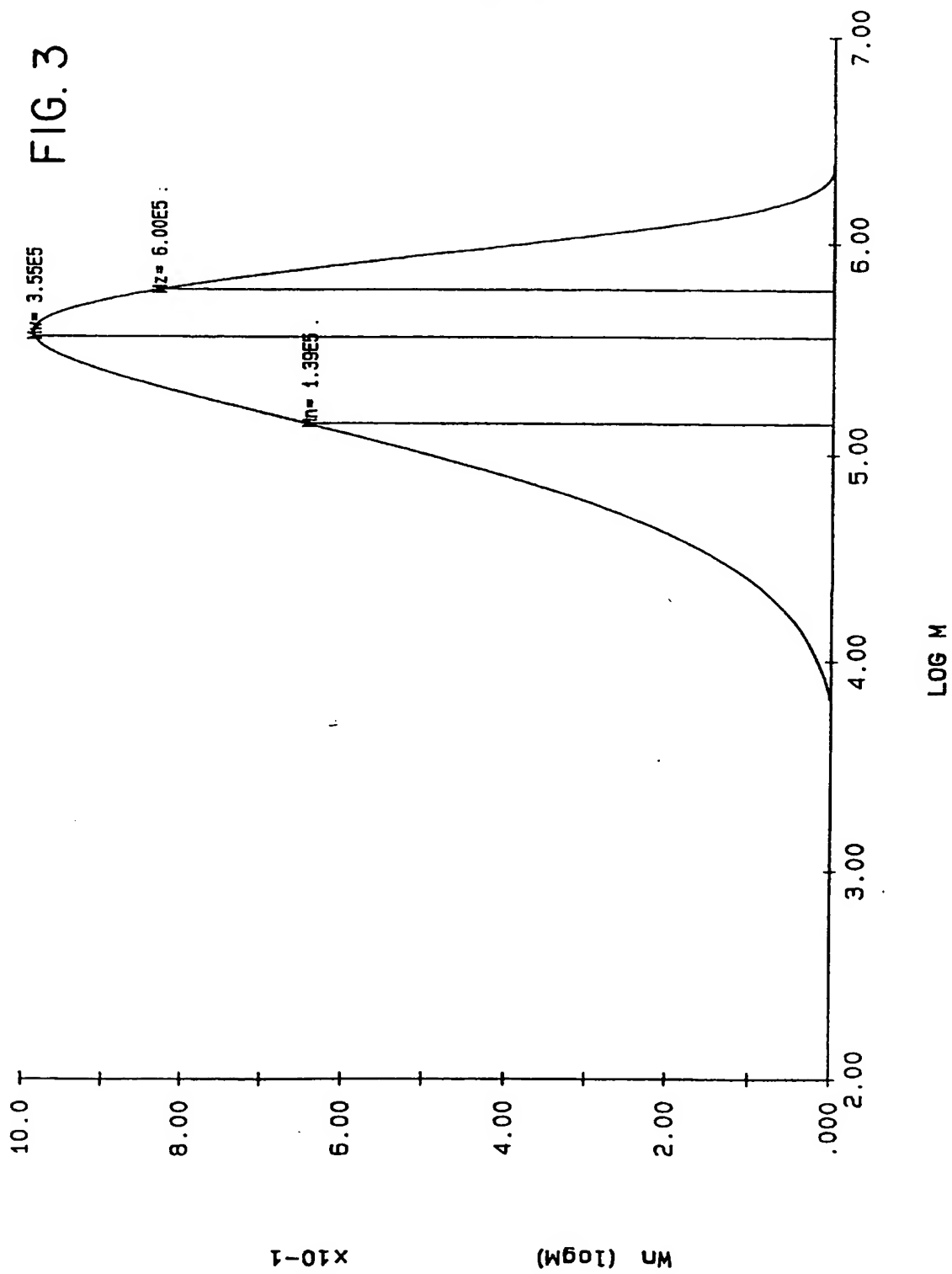
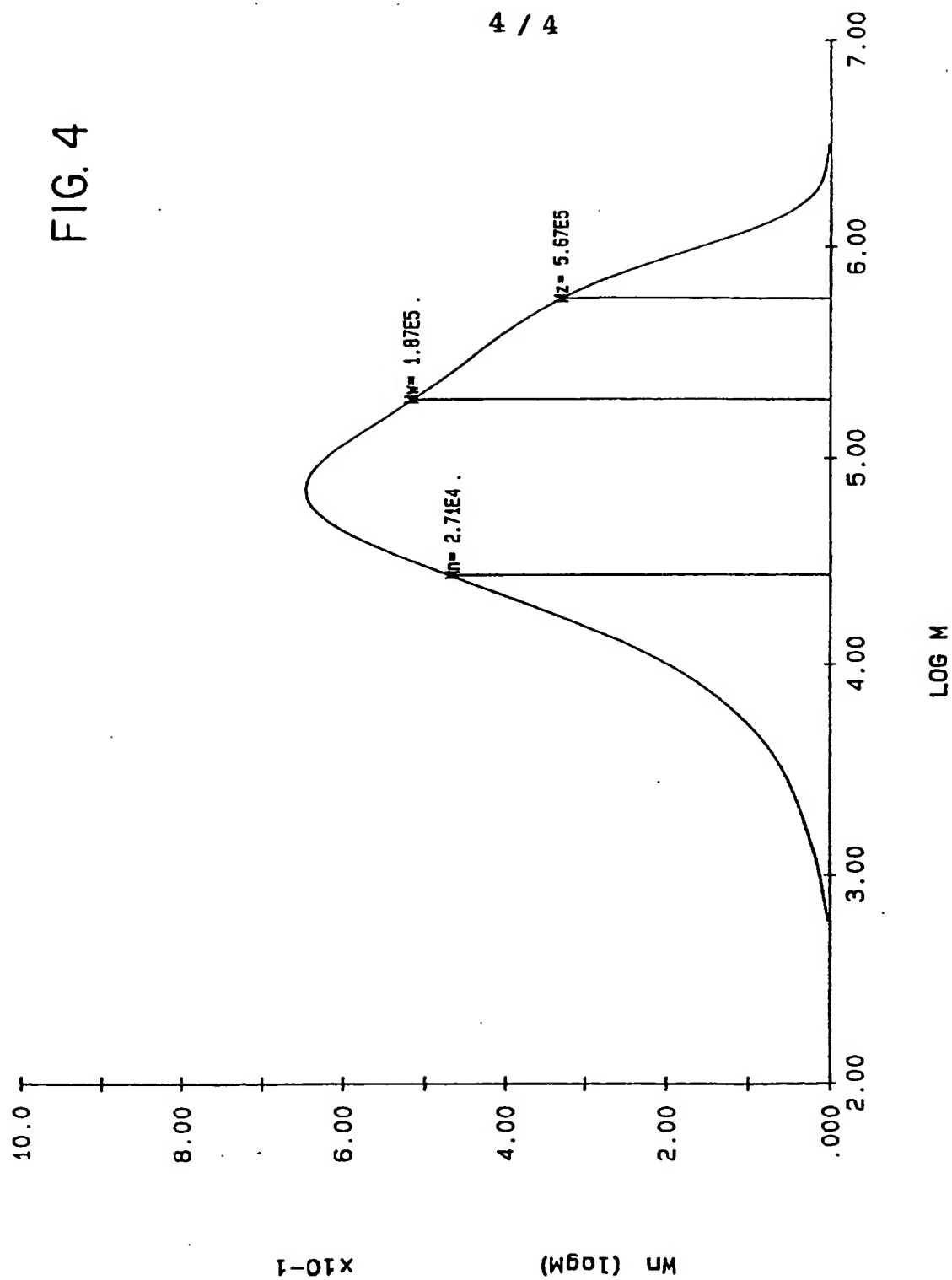


FIG. 2



3 / 4





# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/13148

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C08F10/00 C08F4/652		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search  12 March 1996		Date of mailing of the international search report  21 MARCH 1996
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer  Fischer, B

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Inter:    nal Application No  
PCT/US 95/13148

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